Model-based analysis of photoinitiated coating degradation

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Coatings Research at DTU Chemical Engineering

CHEC Research Center

Research Topics (heavy duty coatings)

- Antifouling coatings for ships
- Anticorrosive coatings (incl. weathering)
- Blade coatings for wind turbines
- Intumescent coatings (fire protection)

People

- 2 professors (faculty)
- 3-5 Ph.D. students
- 2-4 M.Sc. Students
- Collaborators from coatings industry

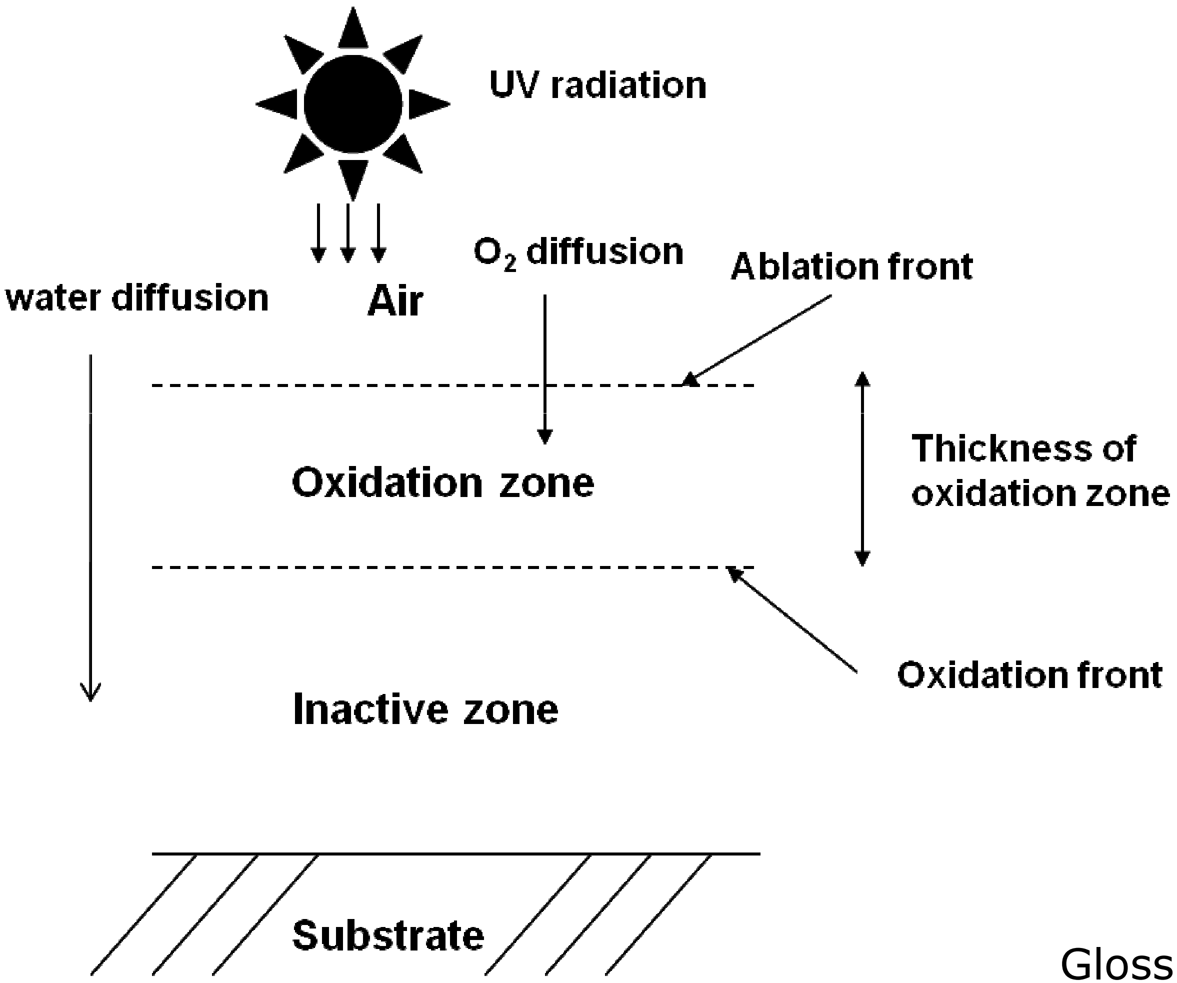
Motivation and topics covered

- To obtain a ”complete” picture of UV-induced coating degradation

- Improve knowledge on interlayer adhesion loss
  – problem between epoxy base coat and PU top coat
  – loss of adhesion after few days of UV exposure

- Contents of presentation
  - mathematical model of coating degradation
  - mechanisms and phenomena included
  - verification
    - high T_g coatings with narrow oxidation zones (2 μm)
    - low T_g coatings with wide oxidation zones (250 μm)
    - effect of light stabilizers
  - future work

Thermoset coating exposed to UV radiation and humidity



Top view:

exposed

unexposed

Gloss loss not considered

Model contents

- Photoinitiated oxidation reactions
- Oxygen permeability
- Water absorption and diffusion
- Reduction of crosslink density (erosion)
- Development of an intrafilm oxidation zone
- Effect of light stabilizers (UV absorber and HALS)

For details on model assumptions see Kiil (2012), JCT Res.

Chemical degradation mechanism

- Case study with crosslinked epoxy-amine coatings

- Closed-loop chemical mechanism

$$E - \mathrm{CC} \xrightarrow{hv} 2\mathrm{R}\cdot \qquad (1)$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot \qquad (2)$$

$$\mathrm{CH_2N} + \mathrm{CHOH} + 2\mathrm{ROO}\cdot + \mathrm{O_2} \rightarrow \mathrm{CON(amide)} + \mathrm{CO(carbonyl)} + \mathrm{H_2O}(l) + 2\mathrm{ROOH} \qquad (3)$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \rightarrow E - \mathrm{CC} \qquad (4)$$

- Reactions not included

$$\mathrm{ROOH} \xrightarrow{hv} \text{volatile end products}$$ Branching

$$\mathrm{ROO}\cdot + \mathrm{ROO}\cdot \rightarrow \mathrm{ROOR} + \mathrm{O_2}$$ Termination (not important here)

Adjustable parameters

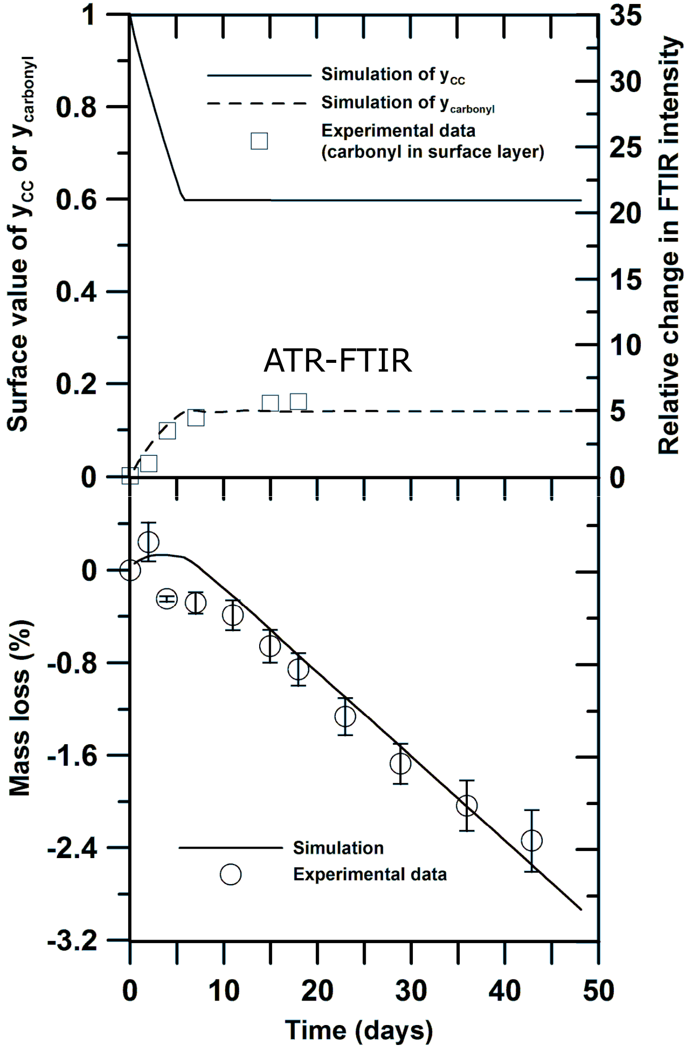
- Rate constants for reaction (1) and/or (2)
  (always included)

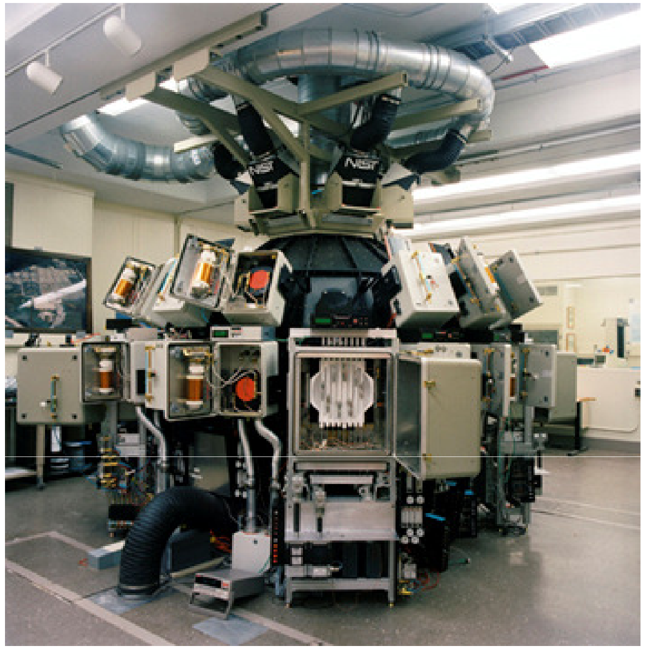
- Diffusion coefficient of oxygen in oxidation zone
  (only when diffusion plays a role)

- Stable conversion of crosslinks at coating surface when erosion is initiated (if erosion takes place)

- Rate constant of radical scavenger
  (only when present)

Simulations and experimental data



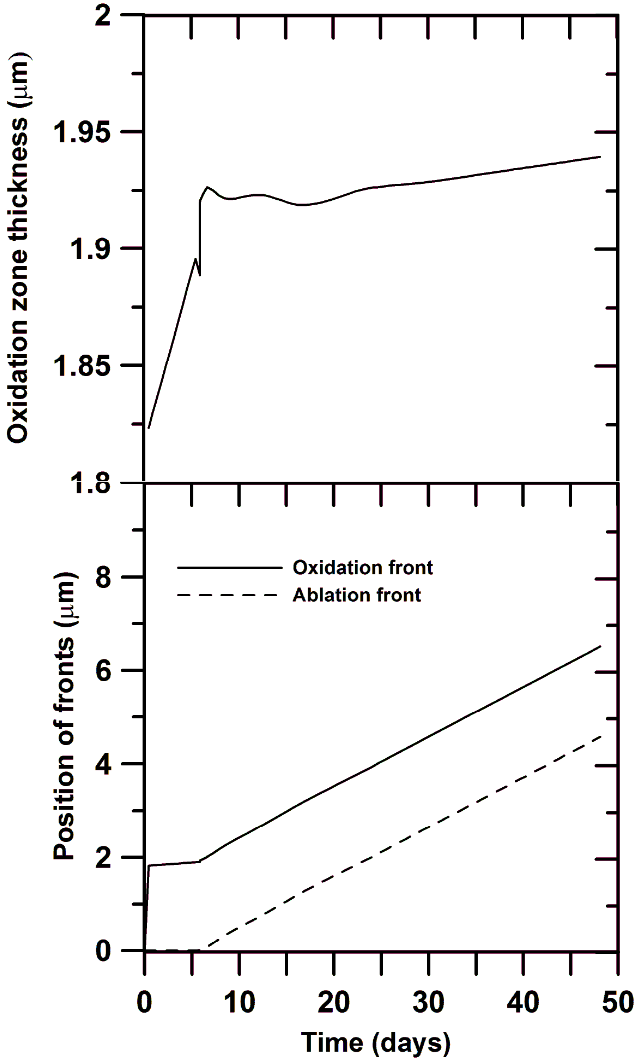


NIST integrating sphere

(data from Nguyen et al., COSI, 2010)

Clear coat, 50 °C, RH=75 %, T_g > 100 °C, UV=480 W/m^2

Simulation of oxidation zone development



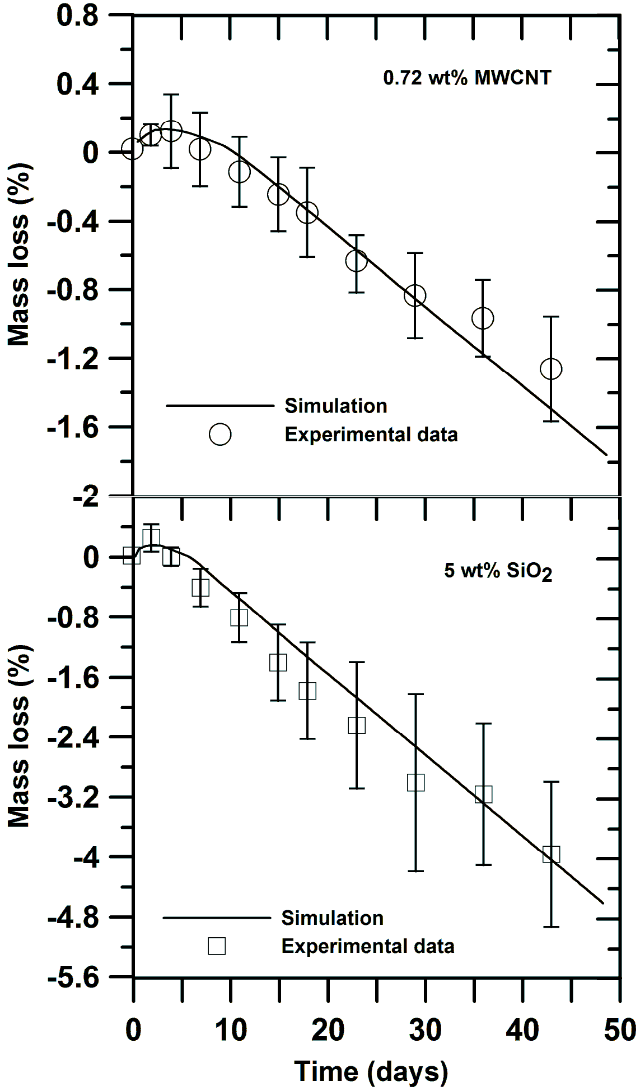
Clear coat, 50 °C, RH=75 %,

T_g > 100 °C, UV=480 W/m^2

Oxygen diffusion very important

Oxidation zone thickness of about 2 μm in agreement with independent measurements by Monney et al. (1997, 1998, 1999)

Effect of nano-pigments on mass loss



50 °C, RH=75 %

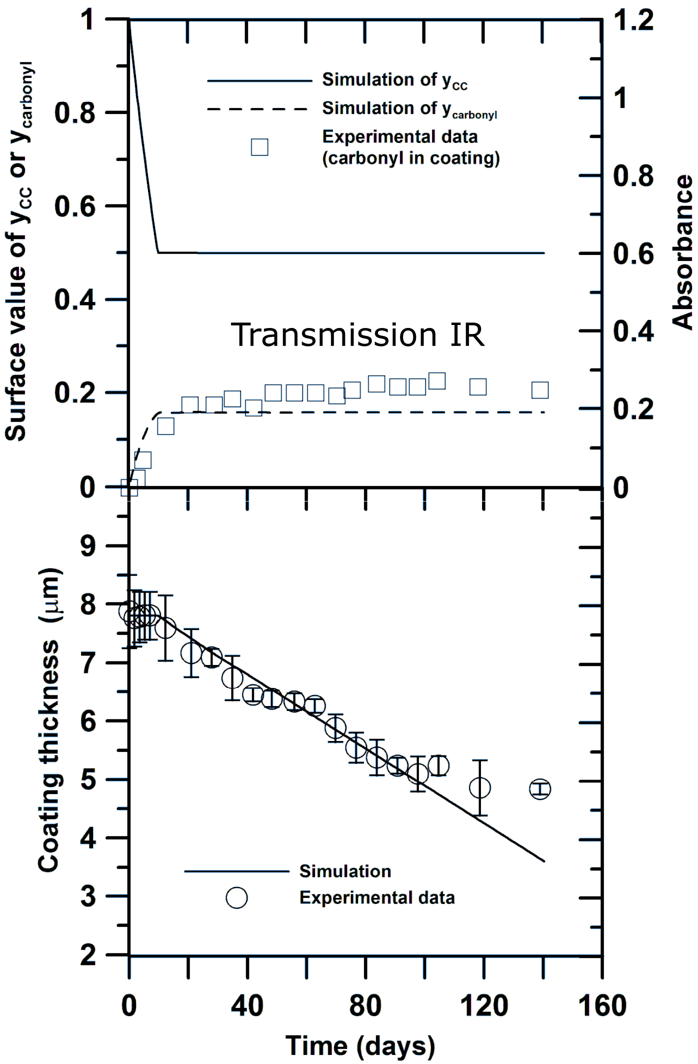
T_g > 100 °C, UV=480 W/m^2

MWCNT has a strong effect on stable surface conversion

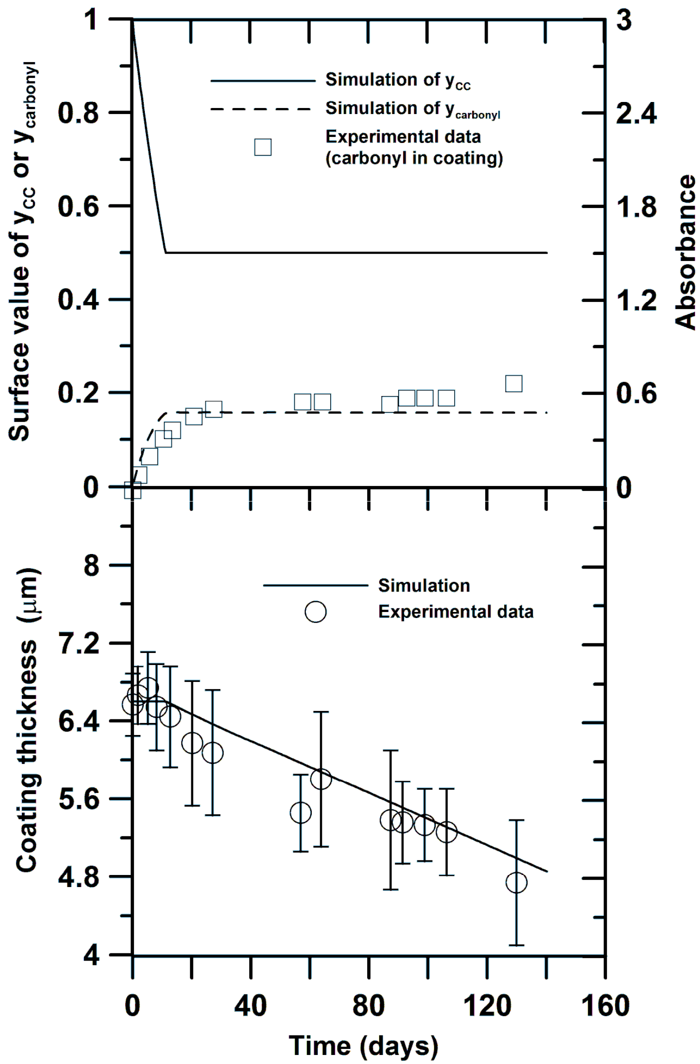
Nano-SiO_2 has no effect (same parameters used as for clear coat)

Experimental data from Nguyen et al., NIST, (2010)

Effect of relative humidity, RH (50 °C), on erosion rate



RH=75 %



RH=9 %

Experimental data from Rezig et al., NIST, (2006) (T_g=123 °C)

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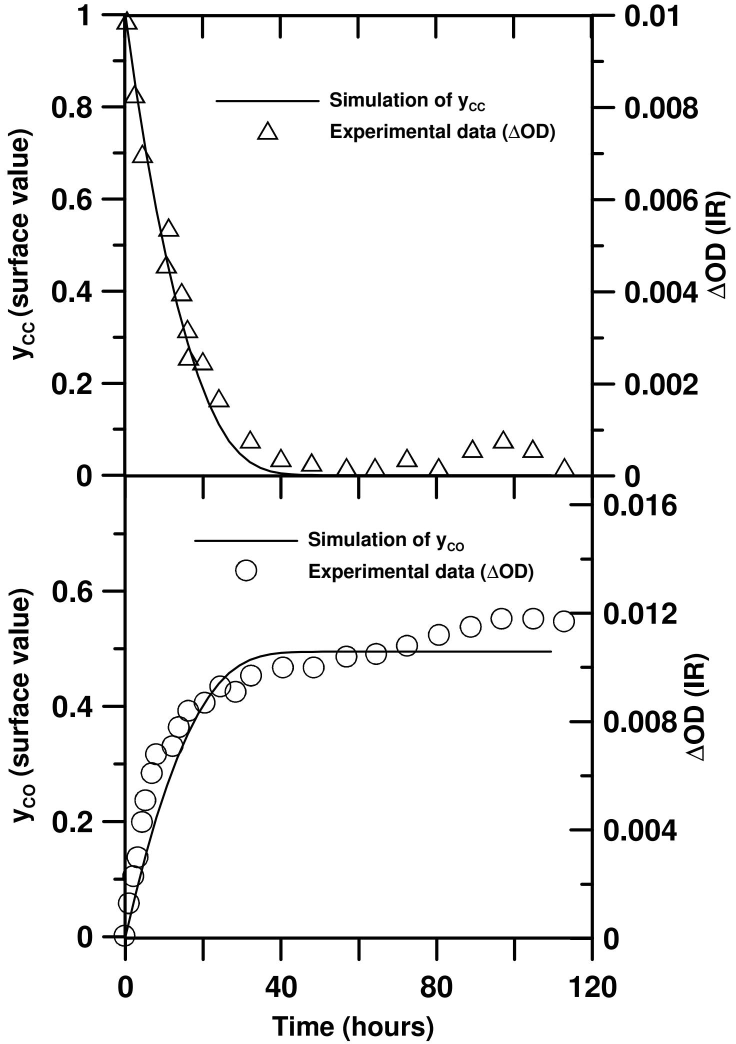
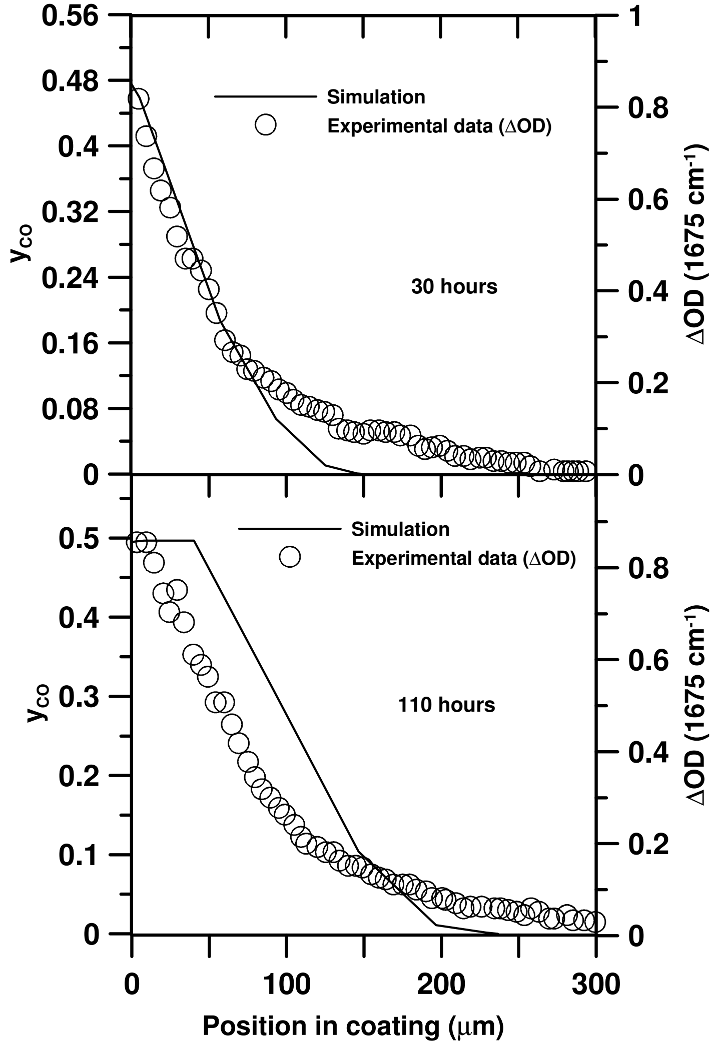
Simulations and experimental data (Mailhot et al., France, 2005)

ATR-IR data

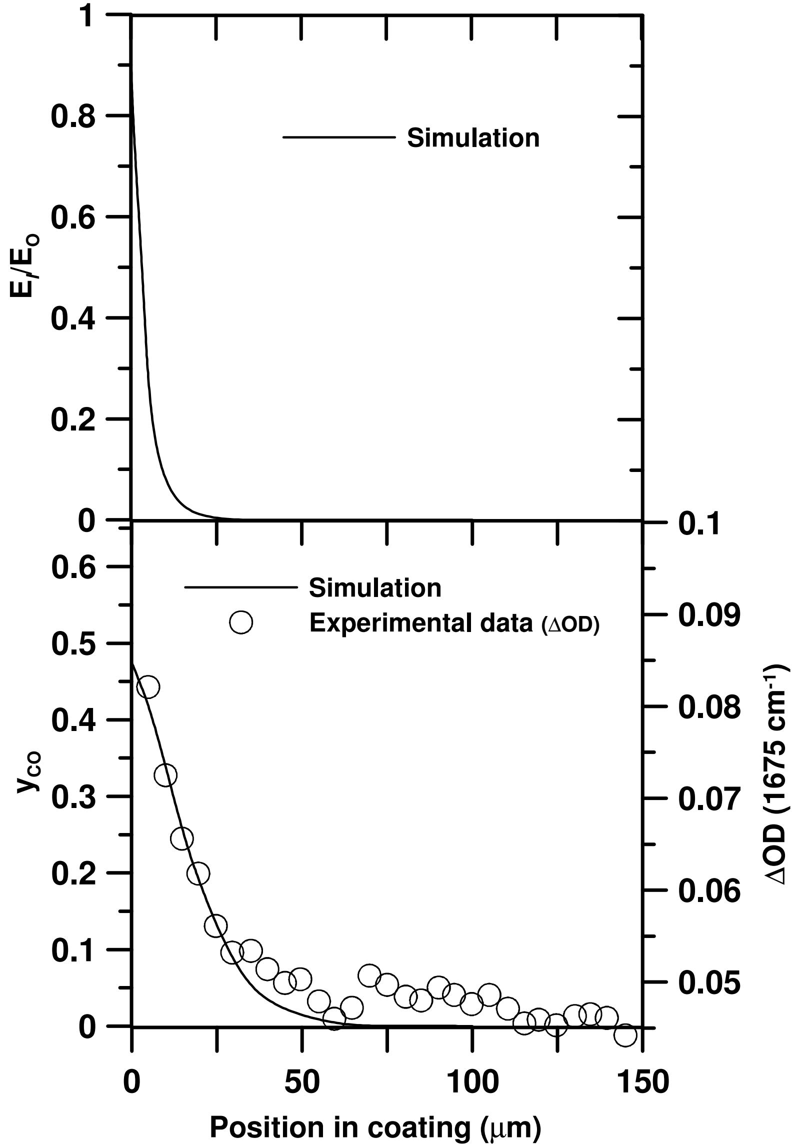


Micro-FTIR data



Clear coat, 60 °C, T_g=-50 °C, RH and UV unknown, no light stabilizers

Effect of UV absorber on absorption and oxidation depth



Clear coat, 60 °C, Tg=-50 °C, 30 hours

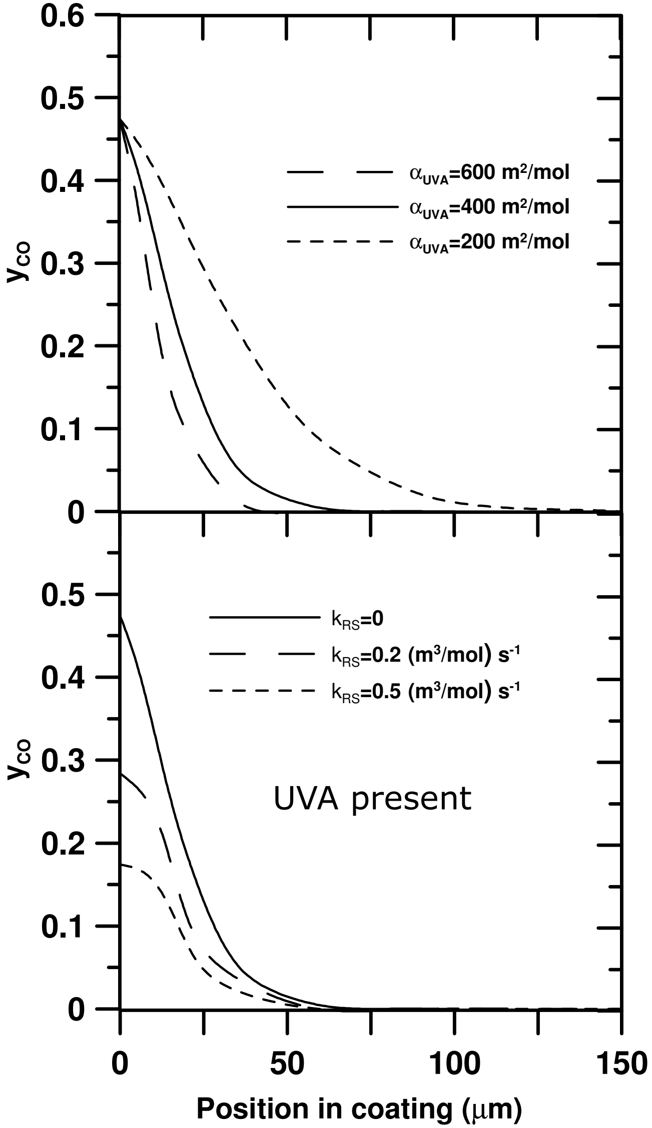
Experimental data from Mailhot et al. (2004)

Without UV absorber the oxidation zone thickness was 250 μm

No oxygen concentration profile

Absorption of UV radiation limits oxidation zone thickness

Effect of molar absorptivity of UV absorber and rate constant of radical scavenger



Clear coat, 60 °C, Tg=-50 °C, 30 hours,

UV absorber present

Reaction of radical scavenger (HALS):

$$R_2NO\cdot + R\cdot \rightarrow R_2NOR$$

$$(-r_{R\cdot}) = k_{RS} C_{R\cdot} C_{R_2NO\cdot}$$

Conclusions

- Mathematical model developed for photoinitiated coating degradation
- The relative importance of the different rate phenomena quantified
- Model requires calibration of adjustable parameters for practical use
  - from laboratory data to service life prediction
- Model cannot predict gloss loss and speciation of photoproducts

Goldschmidt and Streitberger (2007)

Future work

- Extend model to cyclic accelerated testing
  - effects of rain erosion, time of wetness, UV radiation, and temperature
- Extend model to more complex epoxy-amine formulations
  - including other pigments and additives
- Extend model to other coatings/binders
  - requires a closed-loop mechanism and data for model calibration
- Use model for simulation of weather scenarios of commercial interest
- Detailed experimental data series required!

Thank you for your attention...

Financial support by the Hempel Foundation is gratefully acknowledged

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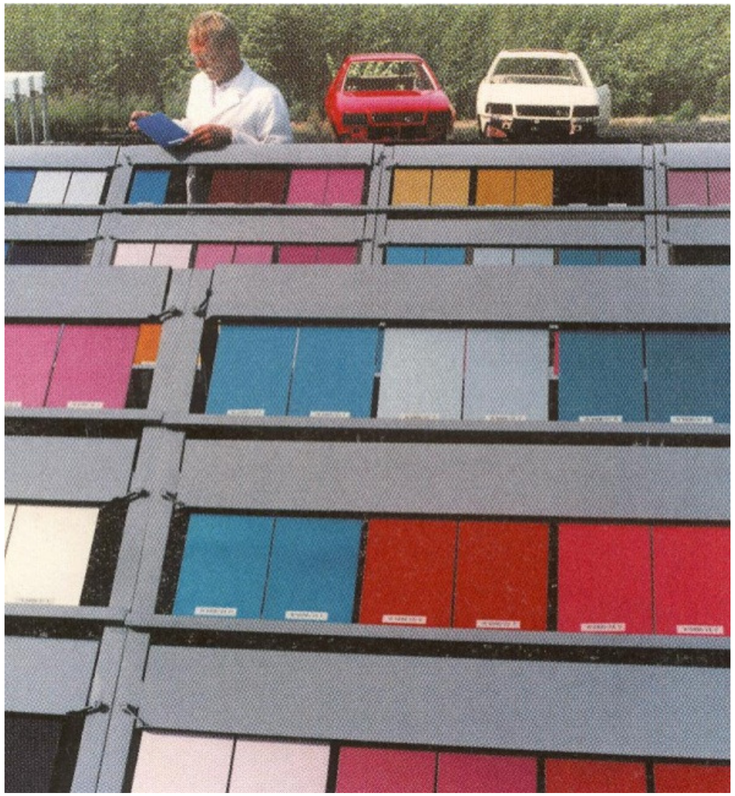

Goldschmidt and Streitberger (2007)